Advanced molecular devices based on light-driven molecular motors

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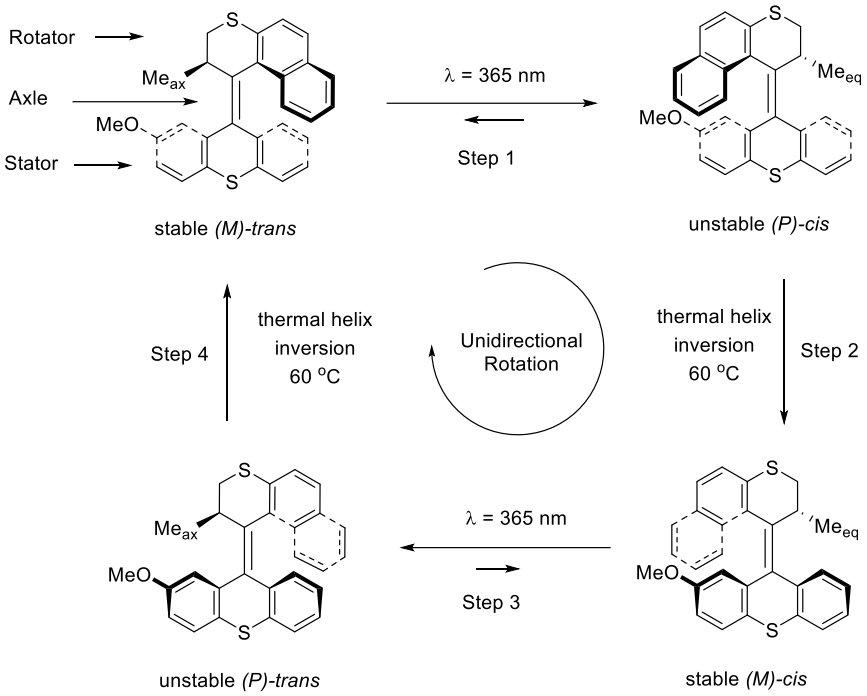
Summary

Nature has provided excellent examples on how to control motion at the molecular level. Most of the molecular machines and devices are capable of operating crucial biological processes with high efficiency and precise control. These fascinating natural molecular machines and devices therefore are major sources of inspiration for nanotechnology. A key challenge in nanotechnology is to build an artificial system that can operate with external stimuli and perform useful works at the molecular level.

Many efforts have been made to address this challenge over the past decades. Directly employing biological motors for applications in biotechnology is one approach. However, the limited condition of using biological motors *ex vivo* leads to the development of synthetic molecular rotors and motors that can operate under external stimuli in a wide range of conditions. Chapter 1 gives a brief review on some characteristic molecular rotors and motors. Among these molecular rotors and motors, molecular motors based on overcrowded alkenes are unique since they are capable of undergoing repetitive unidirectional rotation (Scheme 1). The repetitive unidirectional rotation around the central double bond (the axis of rotation) is achieved by two energetically uphill photochemical isomerization steps (Scheme 1, step 1,3) each followed by an energetically downhill thermal helix inversion step (Scheme 1, step 2,4). In this thesis, the goal is to apply light-driven molecular motors as a tool to control molecular motion and to build advanced dynamic functional systems.



Scheme 1. Unidirectional rotation of a light-driven molecular motor.

Chapter 2 describes a photo-responsive amphiphile based on overcrowded alkene. The amphiphile is able to self-assemble in water with DOPC to form micrometre long and shape consistent end-capped nanotubes. The end-capped vesicle can be reversibly removed and reattached without affecting the tubular structure. The presence of a photoswitchable and fluorescent core in the amphiphilic molecules allows fast and highly controlled disassembly of the nanotubes upon irradiation and distinct disassembly processes to be observed in real-time using fluorescence microscopy.

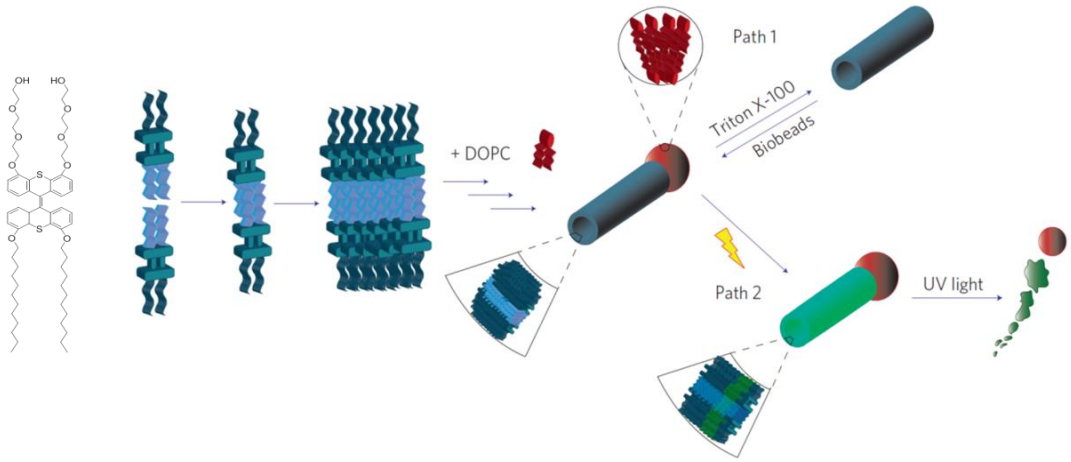


Figure 1. Self-assembly of a photo-active amphiphile.

Chapter 3 focuses on the development of a novel, light-responsive, self-assembled nanotube system based on amphiphilic light-driven molecular motors. Two molecular motors with different rotary speed were designed and synthesized. Both of these motors can self-assemble into distinct nanotubes in water in the presence of DOPC. The slow motor is found to be able to reversibly switch the morphologies of the self-assembled structures between end-capped nanotubes and vesicles upon irradiation or heating.

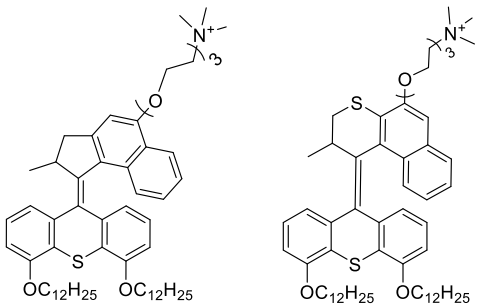


Figure 2. Two amphiphilic light-driven molecualr motors.

In chapter 4 of this thesis, a series of first generation light-driven molecular motors with rigid substituents of varying length is synthesized to act as 'molecular stirrers' (Figure 3). The rotary speed is affected by the rigidity of the substituents and the length of the rigid substituents and that the differences in speed are governed by entropy effects. Most pronounced is the effect of solvent viscosity on the rotary motion when long rigid substituents are present. The □ values obtained by the *free volume* model, supported by DFT calculations, demonstrate that during the rotary process of the motor, as the rigid substituent becomes longer, an increased rearranging volume is needed which leads to enhanced solvent displacement and retardation of the motor.

Figure 3. 'Molecular stirrer' based on a first generation light-driven molecular motor.

Chapter 5-7 mainly focus on the development of a highly functionalized system that allows for direct visualization of rotary motion of a light-driven molecule motor on a surface. Chapter 5 describe the design and the required components of the system. Perylene bisimide (PBI) has been chosen as the fluorescence tag for visualization. Experimental data show that the rotary motion of a motor can be fully preserved when it is connected with a PBI unit *via* a rigid tetramer linker (Figure 4).

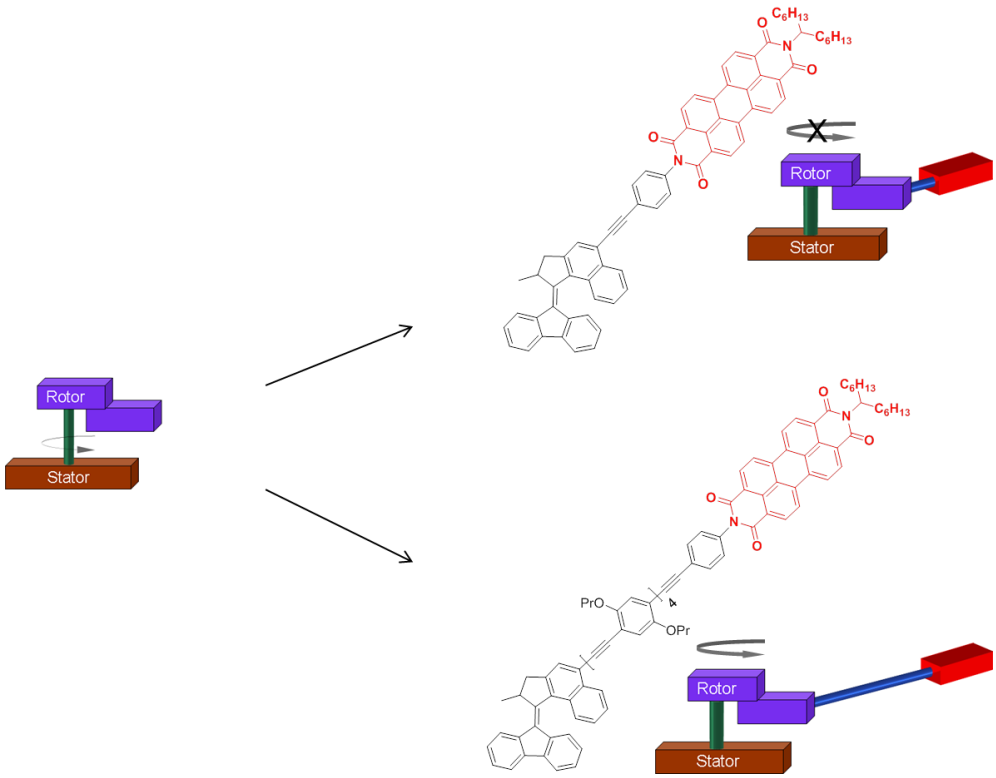


Figure 4. Interactions between PBI unit and molecular motors.

Chapter 6 discusses the synthesis and surface attachment of a highly functionalized light-driven rotary molecular motor (Figure 5a). This motor is obtained by a 34-step synthesis. Incorporation of acetylene legs into the structure allows the motor to be grafted to azide-modified quartz using the “click” 1,3-dipolar cycloaddition reaction. Chapter 7 describes a facile assembly of molecular motors on quartz via non-covalent attachment. The tetra-acid-functionalized motor is bound to an amine-coated quartz surface without prior activation of the acid groups (Figure 5b). Both motors shown in Scheme 3 are equipped with a PBI unit, which allows for the studies of their orientation on surfaces by single molecular defocused wide-field fluorescence microscopy. Both motors show expected polar angles, indicating proper orientations on surfaces.

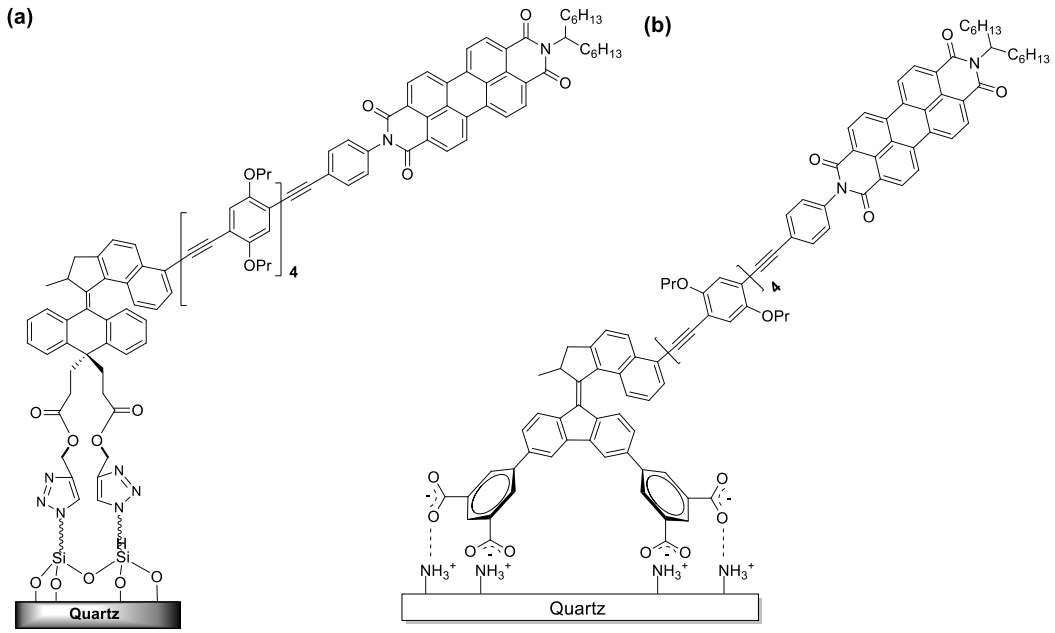


Figure 5. Molecular Motors on surfaces.

In the last chapter of this thesis, a detailed investigation on the photo-controlled formation of chiral textures in sessile droplets of cholesteric liquid crystals was described. By doping the liquid crystal with molecular photo-switches, both optical and structural transitions can be triggered by light, reversibly (Figure 6). Moreover, depending on the initial confinement state of the cholesteric helix, the expression of chirality can be photo-switched on and off by means of an interplay between microscopic and geometric constraints.

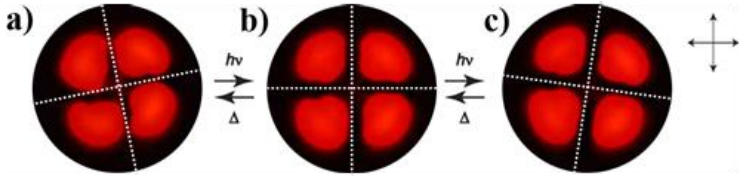


Figure 6. Photo-controlled modification of optical activity in a droplet

Overall, the work presented in this thesis contributes to the development of advanced molecular devices based on light-driven molecular motors. Several multicomponent systems are designed and synthesized. Various spectroscopic techniques are employed to demonstrate that molecular motion can be controlled at molecular level. The insight and knowledge gained will be an important guide for harnessing the controlled molecular motion to perform useful work on the nanoscale and building more advanced functional systems.